EXHIBIT

(21 pages total, including cover)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	:	Attorney Docket No. 2006_1120A
Hiroaki MISAWA et al.	:	**Confirmation No. 1624**
Serial No. 10/585,845	:	Group Art Unit 1713
Filed October 18, 2006	:	Examiner Stephanie P. Duclair
MICRO-FABRICATION METHOD	:	**Mail Stop: AF**

DECLARATION UNDER 37 C.F.R. 1.132

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Sir:

I, Dr. Hiroaki MISAWA, a citizen of Japan, declare:

1. My education history is as follows:

1979 - B.S., Tokyo Metropolitan University

1981 - M.S., The University of Tsukuba

1984 - D.Sc., The University of Tsukuba

2. Attached is my *Curriculum Vitae*, of which the following information details my professional experience:

1984 Post-Doctoral Researcher, The University of Texas.

1986 Assistant Professor, Department of Chemistry, The University of Tsukuba.

1988 Researcher, Microphotoconversion Project, ERATO, Japan Science and Technology Corporation.

1991 Group Leader, Microphotoconversion Project, ERATO, Japan Science and Technology Corporation.

1993 Associate Professor, Faculty of Engineering, The University of Tokushima.

1995 Professor, Faculty of Engineering, The University of Tokushima.

1997 Professor, Graduate School of Engineering, The University of Tokushima.

2003-present Professor, The Research Institute for Electronic Science, Hokkaido University.

2006-2009 Head, Nanotechnology Research Center, The Research Institute for Electronic Science, Hokkaido University.

2009-present Director, Research Institute for Electronic Science, Hokkaido University.

3. Attached is a list of publications that I have authored or co-authored. From this list, I have also attached to this Declaration, research paper no. 30, for the following discussion.

4. I have studied the above-identified application, Serial No. 10/585,845, the Office Action therein dated July 16, 2010, and the references relied upon by the Examiner in rejecting the claims.

5. In order to support the patentability of the presently claimed invention, I present the following information.

The presently claimed invention is a micro-fabrication method which comprises applying a femtosecond pulse laser beam to a plastic material to be processed exhibiting a glass phase transition by heating and having a heat-shrinkage to form laser-processed patterns on the surface of or in the above plastic material to be processed, wherein the formed laser-processed pattern is only scaled down by heat treatment without its shape changed, and then heat-treating the plastic material to be processed at a temperature not lower than a glass transition temperature (Tg) to scale down the formed patterns by heat-shrinkage.

To that effect, in the presently claimed invention, it is important that the plastic material to be processed is applied with a femtosecond pulse laser beam so as to be formed into a laser-processed pattern and that the plastic material in which the laser-processed pattern is formed is heat-treated at a temperature that is not lower than the glass transition temperature (Tg) thereof.

As a result of applying the femtosecond pulse laser beam, owing to the temperature elevation caused by applying the femtosecond pulse laser beam, only the local site that has been processed by applying the femtosecond pulse laser beam shrinks.

Subsequently, the plastic material in which the laser-processed pattern is formed is heat-treated at a temperature that is not lower than the glass transition temperature (Tg) thereof, whereby the formed laser-processed pattern is scaled down through shrinkage resulting from the temperature elevation caused by the heat-treatment.

In other words, applying the femtosecond pulse laser beam induces shrinkage of only the local site processed by the application of the femtosecond pulse laser beam. The formed laser-processed pattern is reduced in size by the subsequent heat treatment at a temperature that is not lower than the glass transition temperature (Tg) and is thus it is scaled down. In the heat treatment, since the part to be processed has been already reduced in size, due to the previous application of the femtosecond pulse laser beam, the formed laser-processed pattern is merely scaled down by the heat treatment, but the shape of the formed laser-processed pattern does not change.

The result could not be anticipated by anyone skilled in the art, as discussed below.

It has been said that processing of a transparent material by the use of a laser having a long pulse width as a light source is thermal processing, but the microprocessing of a transparent material by the use of a femtosecond laser is non-thermal processing.

In other words, it has been said that, in case where a transparent material is processed by the use of a femtosecond laser, there occurs no thermal damage (effect). In fact, a patent, U.S. Patent No. 5,656,186, has been granted for use of non-thermal microprocessing of a transparent material with a femtosecond laser. I also have reported many research papers, utilizing non-thermal microprocessing of a transparent material with a femtosecond laser. As indicated, a list of publications concerning femtosecond laser processing is attached.

Contrary to the above fact, the presently claimed invention has first clarified that, in the microprocessing of a transparent material by the use of a femtosecond laser, only the site processed by applying the femtosecond pulse laser beam shrinks. This is due to the temperature elevation caused by applying the femtosecond pulse laser beam, or in other words, the microprocessing of a transparent material by the use of a femtosecond laser is not a non-thermal treatment.

This fact is unexpected even for one who has heretofore made studies of femtosecond laser processing, and is a fact that could not be anticipated by one skilled in the art. I have reported this in the enclosed research paper no. 30, from the attached list of publications.

From the above, microprocessing of a transparent material by the use of a femtosecond laser is not a non-thermal treatment and could not be anticipated by anyone skilled in the art.

In addition, the fact that the formed laser-processed pattern is only scaled down by heat treatment at a temperature not lower than the glass transition temperature (Tg) without its shape change could not have been anticipated by anyone skilled in the art, and the results from the presently claimed invention are unpredictable.

6. I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Nov. 16, 2010
Date

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Dr. Hiroaki MISAWA

CURRICULUM VITAE

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Educational Backgrounds

1979	B.S. Tokyo Metropolitan University
1981	M.S The University of Tsukuba
1984	D.Sc. The University of Tsukuba

Research and Professional Experience:

1984	Post-doctoral researcher, The University of Texas.
1986	Assistant Professor, Department of Chemistry, The University of Tsukuba.
1988	Researcher, Microphotoconversion Project, ERATO, Japan Science and Technology Corporation.
1991	Group Leader, Microphotoconversion Project, ERATO, Japan Science and Technology Corporation.

1993	Associate Professor, Faculty of Engineering, The University of Tokushima.
1995	Professor, Faculty of Engineering, The University of Tokushima.
1997	Professor, Graduate School of Engineering, The University of Tokushima.
2003-present	Professor, The Research Institute for Electronic Science, Hokkaido University.
2006-2009	Head, Nanotechnology Research Center, The Research Institute for Electronic Science, Hokkaido University.
2009-present	Director, Research Institute for Electronic Science, Hokkaido University.

1998-1999	Representative Researcher, The Core Research for Industry Creation, NEDO Community Consortium Research Development.
2000-2001	Representative Researcher, Community New Technology Creation Research Development, NEDO Community Consortium Research Development.
2001-2007	Representative Researcher, Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation.
2007-2011	Representative, Strong Photon-Molecule Coupling Fields for Chemical Reactions,

	Grant-in-Aid for Scientific Research (KAKENHI) on Priority Area, MEXT, Japan.
2007-2012	HINTS Hokkaido University Representative, Hokkaido Innovation through Nanotechnology Support (HINTS), Nanotechnology Network Project MEXT, Japan

The history of Research:

1984-1987	Engaged in the research on the photochemistry of organic material.
1988-1991	Engaged in the research on microchemistry.
1993-present	Engaged in the research on nano/micro science and technology.

Specific Field: Photochemistry, Laser Process, Nano/Micro Science and Technology.

Awards:

1992 Moet Hennessy Louis Vuitton International Science award.

2005 Japanese Photochemistry Association Award for 2005.

2006 The Chemical Society of Japan Award for Creative Work.

Social Activities (Selected)

2005-2008	Guest Professor, Zhejiang University, China
2006-2007	Executive Director, The Japanese Photochemistry Association
2006-2007	Chairman, NEDO Nanotechnology Road Map "Nano-imprint, Beam-processing" Working Group
2006-Present	Scientific member, the JSPS FoS Symposium Advisory Board
2007-2009	Associate Editor, TNANO (IEEE Transactions on Nanotechnology)
2007-Present	Committee member, MEXT Nanotechnology Network Committee
2008-Present	Secretary, The Chemical Society of Japan Hokkaido Branch
2008-Present	Adviser, JST-PRESTO "Innovative use of light and materials/life"
2009-Present	Editorial Advisory Board Member, ACS Applied Materials and Interfaces
2009-2012	Guest Professor, Xi'an Jiaotong University, China
2010-2012	Advisory Board Member, Journal of Physical Chemistry

List of Publications

Hiroaki MISAWA

1. M. Watanabe, H.-B. Sun, S. Juodkazis, T. Takahashi, S. Matsuo, Y. Suzuki, J. Nishii and H. Misawa,
   "Three-dimenisional Optical Data Storage in Vitreous Silica",
   Jpn. J. Appl. Phys., 37, L1527-L1530 (1998).

2. H.-B. Sun, S. Matsuo and H. Misawa,
   "Three-dimensional Photonic Crystal Structures Achieved with Two-photon-absorption Photopolymerization of Resin",
   Appl. Phys. Lett., 74, 786-788 (1999).

3. S. Juodkazis, H. Ishii, S. Matsuo and H. Misawa,
   "Photoelectrochemical Submicrometer Patterning of Titanium Dioxide by Platinum",
   J. Electroanal. Chem., 437, 235-239 (1999).

4. M. Watanabe, H.-B. Sun, S. Juodkazis, S. Matsuo and H. Misawa,
   "Luminescence and Defects Formation by Visible and Near-infrared Irradiation of Vitreous Silica",
   Phys. Rev. B, 60, 9959-9964 (1999).

5. H.-B. Sun, S. Matsuo and H. Misawa,
   "Microfabrication and Characteristics of Two-Dimensional Photonic Crystal Structures in Vitreous Silica",
   Opt. Rev., 6, 396-398 (1999).

6. M. Watanabe, S Juodkazis, H.-B. Sun, S. Matsuo, H. Misawa, M. Miwa and R. Kaneko,
   "Transmission and Photoluminescence Images of 3D Memory in Vitreous Silica",
   Appl. Phys. Lett., 74, 3957-3959 (1999).

7. K. Yamazaki, S. Juodkazis, M. Watanabe, H.-B. Sun, S. Matsuo and H. Misawa,
   "Recording by Microexplosion and Two-Photon Reading of Three-Dimensional Optical Memory in Polymethylmethacrylate Films",
   Appl. Phys. Lett., 76, 1000-1002 (2000).

8. S. Juodkazis, M. Watanabe, H.-B. Sun, S. Matsuo, J. Nishii and H. Misawa,

"Optically Induced Defects in Vitreous Silica",
Applied Surface Science, 154/155, 696-700 (2000).

9. H.-B. Sun, S. Juodkazis, M. Watanabe, S. Matsuo, H. Misawa and J. Nishii,
"Generation and Recombination of Defects in VitreousSilica Induced by Irradiation with a Near-Infraed Femtosecond Laser",
J. Phys. Chem. B, 104, 3450-3455 (2000).

10. M. Watanabe, S. Juodkazis, H.-B. Sun, S. Matsuo and H. Misawa,
"Two-photon Readout of Three-dimensional Memory in Silica",
Appl. Phys. Lett., 77, 13-15 (2000).

11. H.-B. Sun, T. Kawakami, Y. Xu, J.-Y. Ye, S. Matsuo, H. Misawa, M. Miwa and R. Kaneko,
"Real Three-dimensional Microstructures Fabricated Using Photopolymerization of Resins through Two-photon Absorption",
Opt. Lett., 25, 1110-1112 (2000).

12. M. Watanabe, S. Juodkazis, S. Matsuo, J. Nishii and H. Misawa,
"Crosstalk in Photoluminescence Readout of Three-Dimensional Memory in Vitreous Silica by One- and Two-Photon Excitation",
Jpn. J. Appl. Phys., 39, 6763-6767 (2000).

13. A. Marcinkevicius, S. Juodkazis, M. Watanabe, M. Miwa, S. Matso, J. Nishii and H. Misawa,
"Femtosecond Laser-Assisted Three-Dimensional Microfabrication in Silica",
Opt. Lett., 26, 277-279 (2001).

14. H.-B. Sun, Y. Xu, K. Sun S. Juodkazis, M. Watanabe, S. Matsuo, J. Nishii and H. Misawa
"Arbitrary-Lattice Photonic Crystals Created by MultiPhoton Microfabrication",
Opt. Lett., 26, 325-327 (2001).

15. M. Miwa, S. Juodkazis, T. Kawakami, S. Matsuo and H. Misawa,
"Femtosecond Two-Photon Stereo-Lithography",
Appl. Phys. A, 73, 561-566 (2001).

16. H.-B. Sun, V. Mizeikis, Y. Xu, S. Juodkazis, J-Y. Ye, S. Matsuo and H. Misawa,

"Microcavities in Polymeric Photonic Crystals",
Appl. Phys. Lett., 79, 1-3 (2001).

17. V. Mizeikis, H-B. Sun, A. Marcinkevicius, J. Nishii, S. Matsuo, S. Juodkazis and H. Misawa,
"Femtosecond Laser Micro-fabrication for Tailoring Photonic Crystals in Resins and silica",
J. Photochem. Photobiol. A: Chem, 145, 41-47 (2001).

18. T. Kondo, S. Matsuo, S. Juodkazis and H. Misawa,
"Femtosecond Laser Interference Technique with Diffractive Beam Splitter for Fabrication of Three-Dimensional Photonic Crystals",
Appl. Phys. Lett., 79, 725-727 (2001).

19. A. Marcinkevicius, V. Mizeikis, S. Juodkazis, S. Matso and H. Misawa,
"Application of Bessel Beams for Microfabrication of Dielectrics by Femtosecond Laser",
Jpn J. Appl. Phys., 40, L1197-L1199 (2001).

20. S. Juodkazis, S. Matsuo, H. Misawa, V. Mizeikis, A. Marcinkevicius, H-B. Sun, Y. Tokuda, M. Takahashi, T.Yoko and J. Nishii,
"Application of Femtosecond Laser Pulses for Microfabrication of Transparent Media",
Appl. Surface Science, 197-198, 705-709 (2002).

21. A. Marcinkevicius, V. Mizeikis, S. Juodkazis, S. Matsuo and H. Misawa,
"Effect of Refractive Index-Mismatch on Laser Microfabrication in Silica Glass",
Appl. Phys. A, 76, 257-260 (2003).

22. K. Yamasaki, S. Juodkazis, T. Lippert, M. Watanabe, S. Matsuo and H. Misawa,
"Dielectric Breakdown of Rubber Materials by Femtosecond Irradiation",
Appl. Phys. A, 76, 325-329 (2003).

23. H. Segawa, K. Yoshida, T. Kondo, S. Matsuo and H. Misawa,
"Fabrication of Photonic Crystal Structures by Femtosecond Laser-Induced Photopolymerization of Organic-Inorganic Film",
Journal of Sol-Gel Science and Technology, 26, 1023-1027 (2003).

24. T. Kondo, S. Matsuo, S. Juodkazis, V. Mizeikis and H. Misawa,

"Multi-photon Fabrication of Periodic Structures by Multi-beam Interference of Femtosecond Pulses",
Appl. Phys. Lett., 82, 2758-2760 (2003).

25. E. Vanagas, I. Kudryashov, D. Tuzhilin, S. Juodkazis, S. Matsuo and H. Misawa, "Surface Nanostructuring of BoroSilicate glass by Femtosecond nJ Energy Pulses", Appl. Phys. Lett, 82, 2901-2903 (2003).

26. K. Yamasaki, S. Juodkazis, S. Matsuo and H. Misawa, "Three-Dimensional Micro-Channels in Polymers: One Step Fabrication", Appl. Phys. A. 77, 371-373 (2003).

27. S. Juodkazis, A. V. Rode, E. G. Gamaly, S. Matsuo and H. Misawa, "Recording and Reading of Three-dimensional Optical Memory in Glasses", Appl. Phys., B 77, 361-368 (2003).

28. T. Kondo, K.Yamasaki, S. Juodkazis, S. Matsuo, V.Mizeikis and H. Misawa, "Three-Dimensional Microfabrication by Femtosecond Pulses in Dielectrics", Thin Solid Films, 453-454, 550-556 (2003).

29. E. Vanagas, V. Jarutis, S. Juodkazis, V. Mizeikis, I. Kudryashov, S. Matsuo, H. Misawa and R. Tomasiunas, "Laser-Asisted Microfabrication by Using Gauss-Bessel Pulses: The Evidence of Self-action", Lithuanian Journal of Physics, 43, 4, 243-250(2003).

30. S. Juodkazis, K.Yamasaki, S. Matsuo and H. Misawa, "Glass Transition-Assisted Microstructuring in Polystyene", Appl. Phys. Lett., 84, 514-516 (2004).

31. O. Efimov, S. Juodkazis and H. Misawa, "Intrinsic Single- and Multiple-pulse Laser-induced Damage in Silicate Glasses in the Femtosecond-to-nanosecond Region", Phys. Rev. A, 69, 042903 (2004).

32. A. Takita, M. Watanabe, H. Yamamoto, S. Matsuo, H. Misawa, Y. Hayasaki and N. Nishida, "Optical Bit Recording in a Human Fingernail",

Jpn. J. Appl. Phys., 43, 1, 168-171 (2004).

33. S. Juodkazis, H. Okuno, N. Kujime, S. Matsuo and H. Misawa,
"Hole Drilling in Stainless Steel and Silicon by Femtosecond Pulses at Low Pressure",
Appl. Phys. A, 79, 1555-1559 (2004).

34. S. Juodkazis, K. Yamasaki, V. Mizeikis, S. Matsuo and H. Misawa,
"Formation of Embedded Patterns in Glasses Using femtosecond Irradiation",
Appl. Phys. A, 79, 1549-1553 (2004).

35. H. Segawa, S. Matsuo and H. Misawa,
"Fabrication of Fine-Pitch TiO_2-organic Hybrid dot Arrays Using Multi-photon Absorption of Femtosecond Pulses",
Appl. Phys. A., 79, 3, 407-409 (2004).

36. E. Vanagas, A. Mizuyama, S. Koshihara, S. Juodkazis and H. Misawa,
"Glass Cutting by Femtosecond Pulsed Irradiation",
Society of Photo-Optical Instrumentaion Engineers, 3, 2, 358-363 (2004).

37. V. Mizeikis, K. K. Seet, S. Juodkazis and H. Misawa,
"Three-Dimensional Woodpile Photonic Crystals Templates for Infrared Spectral Range"
Opt. Lett., 29, 17, 2061-2063 (2004).

38. Y. Hayasaki, H. Takagi, A. Takita, H. Yamamoto, N. Nishida and H. Misawa,
"Processing Structures on Human Fingernail Surfaces Using a Focused Near-Infrared Femtosecond Laser Pulse",
Jpn. J. Appl. Phys., 43, 12, 8089-8093 (2004).

39. H. Segawa, J. Tabuchi, K. Yoshida, T. Kondo, S. Matsuo and H. Misawa,
"Periodic Structures of Organic- Titania Hybrid Materials Recorded by Multi-Beam Laser Interference Technique",
J. Sol-Gel. Sci. Tech., 32, 287-291 (2004).

40. S. Matsuo, S. Juodkazis and H. Misawa,
"Femtosecond Laser Microfabrication of Periodic Structures using a Microlens Array",
Appl. Phys.A, 80, 683-685 (2005).

41. K. K. Seet, V. Mizeikis, S. Matsuo, S. Juodkazis and H. Misawa,

"Three-Dimensional Spiral-Architecture Photonic Crystals Obtained by Direct Laser Writing",
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42. E. Vanagas, J.-Y. Ye, M. Li, M. Miwa, S. Juodkazis and H. Misawa,
"Analysis of Stress Induced by a Three-dimensional Recording in Glass",
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43. S. Juodkazis, V. Mizeikis, K. K. Seet, M. Miwa and H. Misawa,
"Two-photon Lithography of Nanorods in SU-8 Photoresist",
Nanotechnology, 16, 846-849 (2005).

44. A. Takita, H. Yamamoto, Y. Hayasaki, N. Nishida and H. Misawa,
"Three-dimensional Optical Memory using a Human Fingernail",
Opt. Exp., 13, 12, 4560-4567 (2005).

45. T. Mizuno, K. Yamasaki and H. Misawa,
"Three-Dimensional Optical Memory in a Photoacid-Induced Recording Medium",
Jpn. J. Appl. Phys., 44, 9A, 6593-6595 (2005).

46. E. Gaizauskas, E. Vanagas, V. Jarutis, S. Juodkazis, V. Mizeikis and H. Misawa,
"Discrete Damage Traces from Filamentation of Bessel-Gauss Pulses",
Opt. Lett., 30,1, 80-82 (2006).

47. K. K. Seet, V. Mizeikis, S. Juodkazis and H. Misawa,
"Spiral Three-Dimensional Photonic Crystals for Telecommunications Spectral Range",
Appl. Phys. A, 82, 4, 683-688 (2006).

48. S. Juodkazis, E. Gaizauskas, V. Jarutis, J. Reif, S. Matsuo and H. Misawa,
"Optical Third Harmonic Generation during Femtosecond Pulse Diffraction in a Bragg Grating",
J. Phys. D: Appl. Phys. 39, 50-53 (2006).

49. T. Hashimoto, S. Juodkazis and H. Misawa,
"Void Recording in Silica",
Appl. Phys. A, 83, 337-340 (2006).

50. T. Mizuno, Y. Tanamura, K. Yamasaki and H. Misawa,

"Three-Dimensional Optical Recording in tert-Butoxycarbonyl-Protected Quinizarin Methacrylate Polymers",
Jpn. J. Appl. Phys., 45, 3A, 1640-1647 (2006).

51. S. Juodkazis, K. Nishimura, H. Misawa, T. Ebisui, R. Waki, S. Matsuo and T. Okada, "Control over the Crystalline State of Sapphire",
Adv. Mater., 18, 11, 1361-1364 (2006).

52. S. Juodkazis, K. Nishimura, S. Tanaka, H. Misawa, E. G. Gamaly, B. Luther-Davies, L. Hallo, P. Nicolai and V. T. Tikhonchuk,
"Laser-Induced Microexplosion Confined in the Bulk of a Sapphire Crystal: Evidence of Multimegabar Pressures",
Phys. Rev. Lett., 96, 166101 (2006).

53. S. Juodkazis, H. Misawa, T. Hashimoto, E. G. Gamaly and B. Luther-Davies,
"Laser-induced Micro-explosion Confined in a Bulk of Silica: Formation of Nano-voids",
Appl. Phys. Lett., 88, 201909 (2006).

54. S. Matsuo, Y. Tabuchi, T. Okada, S. Juodkazis and H. Misawa,
"Femtosecond Laser Assisted Etching of Quartz: Microstructuring from Inside",
Appl. Phys. A, 84, 99-102 (2006).

55. K. K. Seet, V. Mizeikis, S. Juodazis and H. Misawa,
"Three-dimensional Circular Spiral Photonic Crystal Structures Recorded by Femtosecond Pulses",
Journal of Non-Crystalline Solids, 352, 2390-2394 (2006).

56. K. K. Seet, V. Mizeikis, S. Juodkazis and H. Misawa,
"Three-dimensional Horizontal Circular Spiral Photonic Crystals with Stop Gaps below 1 μm ",
Appl. Phys. Lett., 88,221101 (2006).

57. E. G. Gamaly, S. Juodkazis, K. Nishimura, H. Misawa, B. L-Davies, L. Hallo, P. Nicolai and V. Tikhonchuk,
"Laser-matter Interaction in the Bulk of a Transparent Solid: Confined Microexplosion and Void Formation",
Phys. Rev. B, 73, 214101(2006).

58. S. Juodkazis, M. Sudzius, V. Mizeikis, E. G. Gamaly, Y. Liu, O. A. Louchev, K. Kitamura, and H. Misawa,
"Three-dimensional Recording by Tightly Focused Femtosecond Pulses in $LiNbO_3$",
Appl. Phys. Lett., 89, 062903 (2006).

59. T. Kondo, S. Juodkazis, V. Mizeikis, S. Matsuo and H. Misawa,
"Holographic Lithography of Periodic Two- and Three-Dimensional Microstructures in Photoresist SU-8",
Opt. Exp., 14, 17, 7943-7953 (2006).

60. S. Juodkazis, T. Kondo, A. Rode, M. Samoc, B. Luther-Davies and H. Misawa,
"Photo-Structuring of As_2S_3 Glass by Femtosecond Irradiation",
Opt. Exp., 14, 17, 7751-7756 (2006).

61. T. Kondo, S. Juodkazis, V. Mizeikis, S. Matsuo and H. Misawa,
"Fabrication of Three-Dimensional Periodic Microstructures in Photoresist SU-8 by Phase-Controlled Holographic Lithography",
New J. Phys., 8, 250, doi:10.1088/1367-2630/8/10/250 (2006).

62. K. K. Seet, S. Juodkazis, V. Jarutis and H. Misawa,
"Feature-size Reduction of Photopolymerized Structures by Femtosecond Optical Curing of SU-8",
Appl. Phys. Lett., 89, 2, 024106-1 – 024106-3 (2006).

63. S. Juodkazis, K. Nishimura and H. Misawa,
"In-bulk and Surface Structuring of Sapphire by Femtosecond Pulses",
Appl. Surf. Sci., 253, 6539-6544 (2007).

64. T. Hashimoto, S. Juodkazis and H. Misawa,
"Void Formation in Glasses",
New J. Phys., 9, 253, doi: 10.1088/1367-2630/9/8/253 (2007).

65. T. Kondo, S. Juodkazis, V. Mizeikis and H. Misawa,
"Three-dimensional High-Aspect-Ratio Recording in Resist",
Journal of Non-Crystalline Solids, 354, 1194-1197 (2008).

66. S. I. Kudryashov, V. D. Zvorykin, A. A. Ionin, V. Mizeikis, S. Juorkazis and H. Misawa,
"Acoustic Monitoring Microplasma Formation and Filamentation of Tightly Focused

Femtosecond Laser Pulses in Silica Glass",
Appl. Phys. Lett., 92, 101916-(1-3) (2008)

67. E.G. Gamaly, S. Juodkazis, H. Misawa, B. Luther-Davies, A. V. Rode, L. Hallo, P. Nicolai, V. T. Tikhonchuk,
"Formation of Nano-voids in Transparent Dielectrics by Femtosecond Lasers",
Current Applied Physics, 8, 3-4, 412-415 (2008).

68. E. G. Gamaly, S. Juodkazis, V. Mizeikis, H. Misawa, A. V. Rode, W. Z. Krolikowski, K. Kitamura,
"Three-dimensional Write-read-erase Memory Bits by Femtosecond Laser Pulses in Photorefractive $LiNbO_3$ Crystals",
Current Applied Physics, 8, 3-4, 416-419 (2008).

69. S. Juodkazis, V. Mizeikis, M. Sudzius, H. Misawa, K. Kitamura, S. Takekawa, E. G. Gamaly, W. Z. Krolikowski, and A.V. Rode,
"Laser Induced Memory Bits in Photorefractive $LiNbO_3$ and $LiTaO_3$",
Appl. Phys. A, 93, 129-133 (2008). (October)

70. S. Juodkazis and H. Misawa,
"Laser Processing of Sapphire by Strongly Focused Femtosecond Pulses",
Appl. Phys. A, 93, 857-861 (2008). (December)

71. S. Juodkazis, Y. Nishi, H. Misawa,
"Femtosecond Laser-assisted Formation of Channels in Sapphire Using KOH Solution",
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APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 4 26 JANUARY 2004

Glass transition-assisted microstructuring in polystyrene

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(Received 29 July 2003; accepted 21 November 2003)

We report on the use of a *shape transition* process to resize patterns prerecorded inside polystyrene film. The shape transition, which is shrinkage in two dimensions and expansion in the third (the volume is conserved), was brought about by annealing polystyrene above the glass transition temperature. This caused approximately twofold lateral shrinkage and fourfold axial stretching of the film, inside which micrometer-sized patterns had been recorded by femtosecond pulses. The transformation of these patterns corresponded to the macroscopic shape transformation of the film. The shape transition was also used to transform a diffraction grating. This allowed the transformation to be confirmed by the corresponding change in diffraction efficiency. The applicability of the shape transition process to nanofabrication is discussed. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1641182]

Interest has increased lately in nano-/microfabrication which exploits the self-organization behavior of materials to form three-dimensional patterns.[1,2] In some shaping and forming processes, such as sheet forming, a plastic material is, usually, thermally quenched and made into a thin sheet by means of pressure. If the melt is cooled slowly under ambient pressure, the resulting glassy structure of the plastic is much different from the one obtained by fast thermal quenching.[3] The relaxation of quenched material strained into a form of thin film could be exploited for nano-/microfabrication tasks. Here, we report how thermal annealing of sheet-formed polystyrene above the glass transition temperature, T_g, could be used to resize structures recorded inside the material by femtosecond pulses. We call such resizing a *shape transition*, which is shrinkage in two dimensions and expansion in the third, with overall conservation of the volume. Shape transition is a thermally activated process of relaxing stress in plastic that has been compressed and thermally quenched.

For the recording material, we used polystyrene films available commercially from Ukita Ltd. and Acrysunday Co., Ltd., both of Japan. The polystyrene from both manufacturers had the same optical transmission, threshold of femtosecond recording, and glass transition temperature. Polystyrene is available in A4 sheets of 0.2–0.4 mm thickness for stationary use and modeling. Its most common use is illustrated in Fig. 1. A miniature of a color picture drawn on a 0.2-mm-thick polystyrene film (Acrysunday) was made by annealing the sample at 130 °C for 2 min. The glass transition temperature of polystyrene is 100 °C.[3] The shape transition brought about by annealing above T_g caused the sample to shrink laterally by about 2.1-fold [Fig. 1(b)] and to stretch axially by 4.4-fold [Fig. 1(d)]. The corresponding change in volume resulting from the shape transition can be expressed as $V_{\text{after}}/V_{\text{before}} \equiv 1/x \cdot 1/y \cdot z/1 \simeq 99.8\%$, where x, y, and z are the dimensions after the shape transition expressed via fractions of the corresponding dimensions before the transition. Polystyrene films 0.4-mm-thick had a 12% smaller modification of dimensions after annealing, and the extent of modification was marginally dependent on the annealing temperature and duration. This phenomenon, the shape transition, was used to resize patterns recorded inside polystyrene by femtosecond pulses. The size of the voxel (the volume element) recorded by femtosecond pulse can be smaller than the cross section of the focal spot,[4,5] which is determined by diffraction laws and aberrations. Hence, it is possible to trace the shape transition-induced changes of patterns formed of voxels on a submicrometer scale.

The laser setup of fs fabrication was based on an oscillator (Tsunami) with a regenerative amplifier (Spitfire, both from Spectra Physics) operating at 800 nm wavelength and a microscope (Olympus IX70). A PZT stage (Polytec PI) was employed to scan the sample according to preprogrammed fabrication patterns. The pulse energy stability was about 3%. The laser radiation was focused inside the sample by a microscope objective lens of $100^{\times}$ magnification that was set at a numerical aperture (NA) of 1.35 (UplanAPO$100^{\times}$). Direct contact between the sample and the objective lens was achieved with the use of immersion oil. This minimized the aberrations, since the refractive indices of the immersion oil and polystyrene were approximately the same, $n \simeq 1.52$. The actual diameter of a focal spot depends on the truncation ratio of the incident beam at the entrance of the objective lens and the beam's quality factor, and can be evaluated precisely.[4]

Pulse energy was directly measured at the point of irradiation by an energy meter (Laserstar OPHIR) using a solid immersion lens (SIL) according to procedures reported

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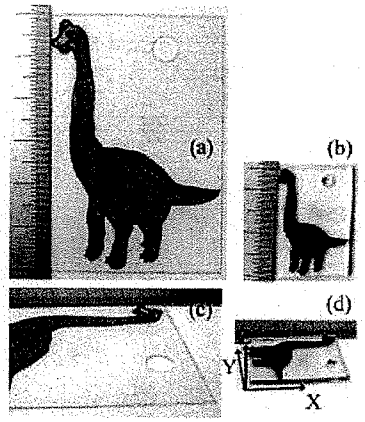

FIG. 1. (Color) Downsizing of a picture drawn on polystyrene (Acrysunday Co., Ltd.) by shape transition, induced by heating the material above the glass transition temperature. Pictures (a), (c) before and (b), (d) after heat treatment at 130 °C for 2 min are shown on the same scale in (a), (b) and (c), (d). The smallest division on the ruler was 0.5 mm.

recently.[6] In order to calculate the recording irradiance at the focus, the pulse duration at the focus was measured by the Grenouille technique[7] (Swamp Optics), and the pulse duration the [full width at half maximum (FWHM)] was retrieved by the frequency-resolved optical gating (FROG) algorithm (Femtosecond Technologies). The pulse duration at the focus was 225±20 fs at a FROG error of less than 2% (more details can be found in Ref. 8).

The spatial dimensions of the pulse focus, a "light pen" used for recording, were close to those evaluated by scalar Debye theory[9] and were (axial×lateral)≈(0.87×0.29) μm^2 (at FWHM) calculated for aberration-free focus inside a medium with refractive index $n=1.5$. Here, the apodization function was chosen to obey the sine condition, which is standard for an aplanatic objective lens.[9] The light intensity at the focus can be calculated from the point spread function (PSF), which defines the electric field amplitude at the focus. For focus of a high numerical aperture lens, the PSF can be found from Debye theory and is given by

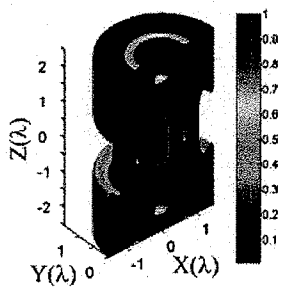

FIG. 2. (Color) Normalized light intensity distribution $I=|E(\upsilon,u)|^2$ [Eq. (1)] in the focus of an aplanatic objective lens with NA=1.35. The dimensions are given in units of λ. The intensity threshold of the isosurface (shown in gray) was set at 1%.

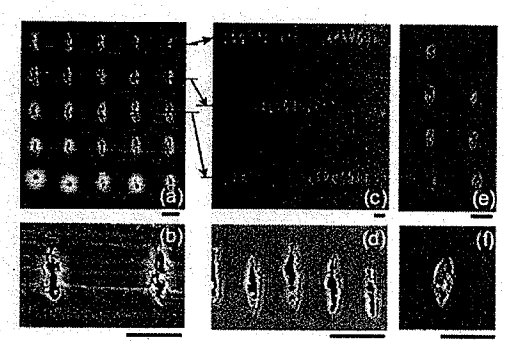

FIG. 3. SEM side-view images of the 0.2-mm-thick polystyrene film (Acrysunday Co., Ltd.) (a), (b) after recording, (c), (d) with subsequent annealing, and (e), (f) after recording into the annealed material. The recording irradiance was about 1.25×LIDT. Annealing was carried out at 135 °C for 100 s. The scale bars are equal to 1 μm.

$$E(\upsilon,u)=\frac{2\pi i}{\lambda}\exp(-ikz)\int_0^{\alpha}P(\theta)J_0\left(\frac{\upsilon\sin(\theta)}{\sin(\alpha)}\right)\times\exp\left(\frac{iu\sin^2(\theta/2)}{2\sin^2(\alpha/2)}\right)\sin(\theta)d\theta, \quad (1)$$

where $\upsilon=kr\sin(\alpha)$ and $u=4kz\sin^2(\alpha/2)$ are the lateral and axial optical coordinates, respectively, $k=2\pi/\lambda$ is the wave number defined by wavelength λ at the focus, J_0 is the zero-order Bessel function of first kind, and α is the half-cone angle of focus. The numerical aperture in material with refractive index n is NA$=n\sin(\alpha)$, and $P(\theta)=\sqrt{\cos(\theta)}$ is the apodization function that satisfies the sine condition (aplanar focusing). The result of the calculation by Eq. (1) is plotted in Fig. 2, showing that the axial focal length was approximately 2.95 times larger than the lateral one at FWHM under our experimental conditions; i.e., the aspect ratio was $f_a\simeq 3$.

The dimensions of the void that had been optically recorded in polystyrene by a single laser pulse were measured by a field emission scanning electron microscope (SEM) (JEOL JSM-6700FT). A Pt film with thickness of a few nanometers was evaporated for SEM observation after the sample was sliced by a biomicrotome (Ultracut UTC), which allowed the soft material to be cut without distortion of the internal features. The cutting procedures were ruled out as a

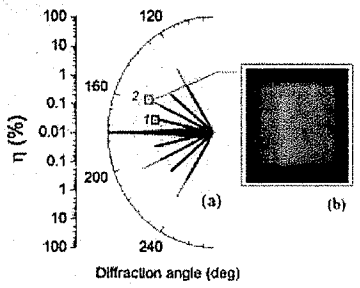

FIG. 4. (Color) (a) Diffraction efficiency, η, vs the diffraction angle, θ [see Eq. (2)] for wavelength λ=532 nm. Theoretical and experimental data are plotted for the gratings: (1) as recorded and (2) after the shape transition. The experimental efficiency was calculated as $\eta=(I_1/I_1+I_0)$, where I_1 and I_0 are intensities diffracted into zeroth and first order, respectively. (b) Image of the 2×2 mm^2 structure taken under white light reflection.

cause of any artifacts in the SEM images. As a reference, the sample after annealing was also irradiated to observe the typical morphology and size of the voxel recorded by a femtosecond pulse. These results are summarized in Fig. 3, where the cross sections along the recording beam propagation are examined. Voids were formed at the focus. These voids should be surrounded by densified cladding of displaced material as we observed inside polymethylmethacrylate.[5] The mechanism of void formation by a single femtosecond pulse is as follows:[10] at dielectric breakdown, when a highly conductive (metallic) state of material is formed at the pulse front, the ensuing pulse energy is absorbed within the skin depth. The absorbed energy surpasses the binding energy and a formed high-pressure gaseous plasma eventually creates voids.

The lateral shrinkage and axial expansion of the polystyrene sample were confirmed to follow precisely those observed macroscopically [in Figs. 1(a)–1(c), the transition marked by arrows], i.e., the same ratio of resizing was observed on an outer perimeter of the sample. The dimensions of the voids recorded at the intensities close to the light-induced damage threshold (LIDT) $1.25\times I_{\mathrm{LIDT}}$ in polystyrene were approximately 0.25 μm in diameter and 1 μm in length. The LIDT in terms of pulse energy was 8.5 nJ, the fluence was 4.5 J/cm^2, and the irradiance was 20 TW/cm^2 (FWHM). The shape transition was found to not significantly change the cross section of the voids [Figs. 3(b) and 3(d)], whereas the intravoid distances followed macroscopic scaling precisely (Fig. 1). Since the shape transition conserved the volume, and the optical transmission was found to be unchanged (within an error of margin of less than 10%), we can assume that the refractive index and absorption coefficient of the material were also unaffected.[11] This is because the mass density remained constant. It is instructive to compare the dimensions of voids recorded in untreated versus annealed polystyrene. Recording in the annealed polystyrene [Figs. 3(e) and 3(f)] resulted in voxels with an internal void of 0.92×0.36 μm^2 cross section (the corresponding aspect ratio was $f_a=2.6$) at 10 μm depth, when the pulse energy was approximately $1.25\times I_{\mathrm{LIDT}}$. These dimensions of the recorded voxels are comparatively close to the focal size derived from Debye theory (Fig. 2). On the other hand, the aspect ratio of the void recorded in the polystyrene was $f_a=4$ [Fig. 3(b)] and it rose to 4.7 [Fig. 3(d)] after annealing. These values are considerably larger than the expected aspect ratio of the focal spot.

The larger f_a values of voids recorded in polystyrene before annealing can be explained by local heating during dielectric breakdown, which caused the shape transition to take place in localized fashion. It is worth noting that the recording power per pulse at LIDT was just 38 kW, much lower than the critical power of self-focusing, which is about 1–2 MW for glassy materials. This is the reason why this laser recording can be considered *direct laser writing*.[12] That is, photomodification of the material is expected to closely follow the proportions of the light intensity distribution at the focus. A slightly larger aspect ratio of voids compared to the ideal focal spot can also be caused in part by aberrations.[13]

The shape transition process was applied to resize a diffraction grating recorded in polystyrene by scanned femtosecond pulses. The intensity of diffraction into zeroth and first order was measured. Figure 4 shows the experimental and calculated diffraction efficiencies. The diffraction efficiency was calculated as that of a multislit according to[14]

$$\frac{I}{I_i}=\left(\frac{\sin\beta}{\beta}\right)^2\left(\frac{\sin(N\gamma)}{N\sin\gamma}\right)^2, \tag{2}$$

where I_i and I are the intensity of incident and transmitted light, respectively, N is the number of slits, and the phase parameters $\beta=\frac{1}{2}kb\sin\theta$ and $\gamma=\frac{1}{2}kh\sin\theta$ are determined by the opening length b, the period h, the wave vector $k=2\pi/\lambda$, the wavelength λ, and the diffraction angle θ. Since the Eq. (2) describes the angular dependence of the diffraction efficiency for a transmission grating, the theoretical simulation should be considered quantitative. Shrinkage of a 2.5 μm period grating with an approximately 0.3 μm void at the core upon the shape transition was confirmed qualitatively by measuring the diffraction efficiency (Fig. 4), where theoretical curves were calculated for a 10-slit grating by Eq. (2). As one can see, a twofold decrease of the grating period did indeed increase the diffraction efficiency, and the diffraction angle became twofold larger as expected. This experiment confirms the principle and demonstrates that the shape transition could be useful for photonic applications.

Femtosecond laser fabrication is capable of recording voids and channels in polymethylmethacrylate with cross-sectional dimensions of about 0.4 μm, as we reported earlier.[5] Thus, one can expect that nanostructuring of polymers with feature size of about 100 nm is within reach for femtosecond microfabrication.

In conclusion, we have demonstrated the possibility of resizing a recorded pattern in polystyrene by annealing it above the glass transition temperature. The dimensions of voids recorded in polystyrene were found to be almost unchanged after the shape transition.

This work was supported by the SVBL of the University of Tokushima, by Contract No. F62562-03-P-0208 AOARD 02-35, and JEOL . The drawing of Fig. 1 was made by S. Hase.

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